

Method for Determining H_2SO_4 in Automobile Exhaust

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A relatively simple procedure for measuring H_2SO_4 in auto exhaust will be presented. The system is compatible with the Federal constant volume sampler (CVS unit). The time required to get sufficient sample for titration is 15-30 min. Values on sulfates in exhaust with a catalyst car and a noncatalyst car agree well with literature data obtained by dilution tube and filtration techniques.

Introduction

The reported finding of sulfuric acid (H_2SO_4) in the exhaust of cars equipped with oxidation catalysts has prompted considerable action by industry and government agencies. A number of programs have been reported on to date showing the effects of operating conditions, fuel sulfur levels, and catalyst type on the amount of H_2SO_4 formed. Several sampling systems and analytical methods have been employed in these studies. A modification of the Federal Testing Procedure for H_2SO_4 and sulfur dioxide from stationary sources has been used by a division of the Environmental Protection Agency (EPA). Esso (1) and Ford (2) reported on data obtained by using dilution tubes together with filter systems for collecting exhaust particulates with subsequent analysis of the particulate for sulfate.

This paper describes a method being developed by Chevron Research for sampling and analyzing auto exhaust for sulfate. In approaching the problem, three primary ob-

jectives were set: that the method be compatible with the use of the constant-volume sampler (CVS unit) specified for emissions testing by the EPA; that the analysis be reasonably quick and simple; and that it be specific for sulfate.

Based on the above considerations, a sampling system as shown schematically in Figure 1 was set up. A conventional CVS unit was used to draw outside dilution air in through a paper filter and charcoal bed. The

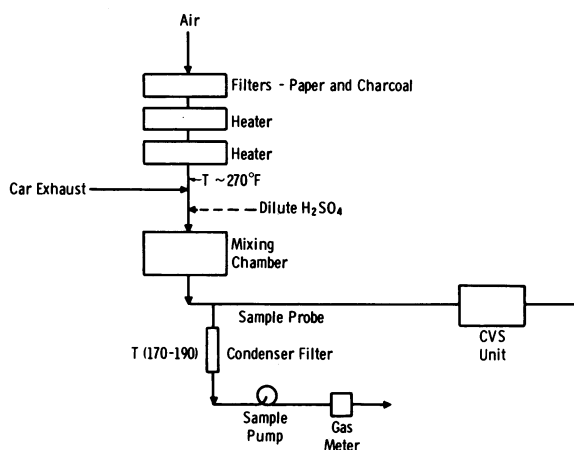


FIGURE 1. Schematic sampling system.

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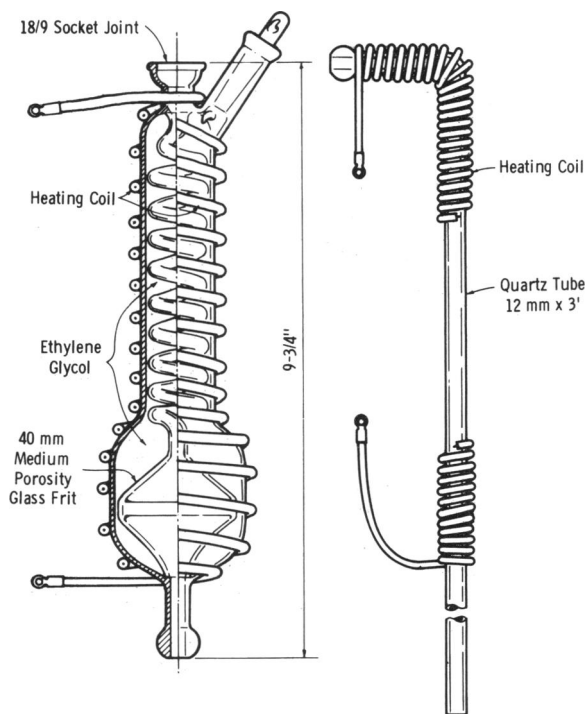


FIGURE 2. Sample probe and condenser filter.

air then passed through two heaters in series, exiting at a temperature of about 270°F. Car exhaust was then brought into the system and the dilution air and exhaust passed into a mixing chamber. The mixing chamber and the ducting between the heaters and the mixing chamber were insulated to minimize heat losses. Approximately 1 ft downstream from the mixing chamber a sample probe was inserted about one-third of the way into the 6-inch duct. The sample probe is connected to a heated condenser filter. Figure 2 shows the design of the probe and the condenser filter. This basic design has been described by Lisle and Sensenbaugh (3). The sample probe consists of a quartz tube. The portion of the probe outside of the duct is wrapped with heating tape and heated to approximately 300°F. This probe is connected to the heated condenser filter. The gas sample enters the condenser and passes through a coil of 1/4-in. tubing downward through a chamber containing a medium-sintered glass frit. The sample then passes out of the condenser to the sample pump and meter for

measuring sample volume. The jacket surrounding the coil and frit is filled with ethylene glycol. A heating cord (Cole Parmer 2/33-6, Flexi-Coil) is wrapped around the jacket to heat the entire apparatus. Silicone rubber cement is used to hold the heating coil in place. During a typical test run, the condenser is preheated to approximately 180°F and held at that temperature during collection of sample. Sample gas is pulled through the apparatus at about 0.2 CFM. The sample drawn for sulfate analysis represents less than 0.1% by volume of the total sample going to the CVS unit. Thus, a regular CVS procedure can be used to measure simultaneously the exhaust hydrocarbons, carbon monoxide, and oxides of nitrogen.

The reasoning for placing heaters on the inlet air system was to avoid the possibility of the sulfur trioxide vapors converting to H₂SO₄ aerosol. If an aerosol were to form, the collection techniques to ensure a representative sample would become complicated; and there was the concern that wall losses would be a serious problem. Our initial estimates were that sulfur trioxide might exist in the exhaust gases at concentrations ranging from about 1–50 ppm. After mixing with the dilution air, the maximum expected concentration would be about 10 ppm. Referring

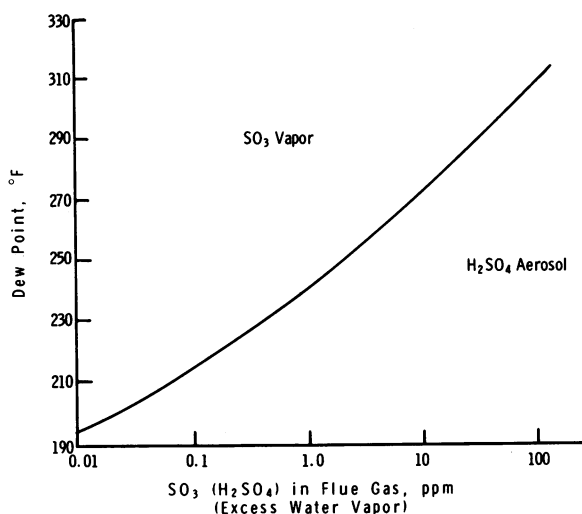


FIGURE 3. SO₃-H₂SO₄ vs. temperature (excess water vapor).

to Figure 3, it is seen that a temperature of 272°F is needed to keep sulfur trioxide in the vapor state in the presence of excess water vapor (3).

Analytical Procedure

After passing from about 3–6 ft³ of sample gas through the condenser filter, the unit is disconnected and taken to the chemical laboratory. After washing out the bottom chamber below the frit to remove condensed water which may contain sulfur dioxide, the condenser is washed out with 5% isopropyl alcohol. The isopropyl alcohol is used to decrease the surface tension to provide better washing. The solution is then titrated with barium ions (barium perchlorate) to determine the amount of sulfate ions. Thorin methylene blue is used as the endpoint indicator. The titration procedure used is similar to that described in ASTM D 2785–70. Blanks were obtained of the wash solution by concentrating a large volume by evaporation.

Checking System and Data

To date, a few steady-state tests have been made on a car equipped with a bead-type platinum catalyst. Tests were also run on the vehicle without the catalyst. In addition, internal checks have been made by injecting a known amount of dilute H₂SO₄ into the sampling system. Extensive checking and testing have not been accomplished to date with this method, but we find the preliminary results sufficiently encouraging to believe that the method has merit and can be run rather simply.

The method for the internal checking was to inject 12 ml of a dilute H₂SO₄ solution (16.34 mg H₂SO₄/ml solution) into the air stream ahead of the mixing chamber (Fig. 1). This solution passed through a quartz chamber heated to ca. 725°F to vaporize the acid. An all-glass and Teflon system was used to inject the sample. Nitrogen at 1 CFM was used to sweep the gases from the heated quartz chamber. The injection was

Table 1. Internal calibration.

	Test 1	Test 2
Conditions		
Temperature at sample probe, °F	271	272
Flow through condenser filter, ft ³	4.708	4.167
Flow rate through CVS unit, ft ³ /min	255	255
Sampling time, min	31	31
Measured H ₂ SO ₄ from filter, µg	90	107
Theoretical amount to filter, µg	117	103
Efficiency of collection, %	77	104
Acid strength (H ₂ SO ₄), mg/ml		16.34
Injection of acid		
Solution injected, ml		12
Temperature of injector tip, °F		≈725

made over a 31-minute period. During this time, the car exhaust system is disconnected and blocked off from the rest of the sampling train. The CVS unit is operating normally. Table 1 shows the results of two internal calibration runs. These results showed that the sampling and analytical methods combined gave a 77% and 104% collection efficiency of the amount of acid injected into the system.

An early question on the use of the method described was whether sulfur dioxide would interfere with the analysis. To check on this point, runs were made with a car having a normal exhaust system (no catalyst). The results of two tests are shown on Table 2. One test was at 50 mph steady state, and the second test included two back-to-back runs of the 1972 Federal Test Procedure starting with a fully warmed-up car. The results show about a 1% indicated conversion of fuel sulfur to sulfate. This result indicates strongly that no significant amount of sulfur dioxide was being trapped in any water phase in the condenser filter. The 1% level of sulfate agrees very well with the reported (1,2) literature levels of 0.5–2.0% sulfate from noncatalyst cars.

The data we have to report on from cars with catalyst are shown also in Table 2. Two steady-state runs at 30 and 50 mph showed approximately the same amount, 0.13 g/mile, of sulfate. These quantities represented a

Table 2. Exhaust measurements with 0.06% sulfur fuel.

Test conditions	Catalyst	Sample probe temperature, °F	Sample time, min	Measured H ₂ SO ₄ , g	H ₂ SO ₄ , g/mile	Conversion of sulfur to H ₂ SO ₄ , %
50 mph	No	385	39	72	0.004	1.2
Two cycles, 1972 FTP—hot start	No	298–360	45.75	39	0.00r	0.9
30 mph	Yes	315	30	1.102	0.128	42.0
50 mph	Yes	430	15	1.462	0.131	39.5

39% conversion of sulfur to sulfate for the 50-mph test and a 42% conversion rate for the 30-mph test. Both of these tests were made after the vehicle had run for several hours at the designated test condition. We have some evidence that it requires two or more hours running before this particular catalyst system comes to a steady state condition. Again, our measured conversions are in reasonable agreement with Esso's reported (1) 25–40% conversion rates for several different systems and cars that they reported on.

Future Work

More work is needed to fully establish this

method as to accuracy and repeatability. On-going work should also include the measurement of sulfur dioxide passing through the condenser-filter so that a material balance can be made on total sulfur. This testing should include evaluations at both steady state and cycling (1972–1975 Federal Test Procedure) conditions.

REFERENCES

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2. Pierson, W. R., et al. Sulfuric acid aerosol emissions from catalyst-equipped engines SAE Preprint 740287 (February 1974).
3. Lisle, E. S., and Sensenbaugh, J. D. Combustion, 36: No. 7, 12 (1965).